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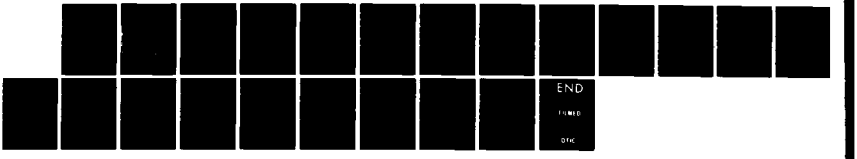

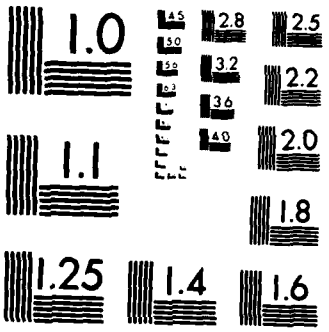

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RHEOLOGY OF DISSEMINATION
PHASE I

by E. A. Kearsley

RHEOLOGY RESEARCH

Gaithersburg, Maryland 20879

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October 1984

US Army Armament, Munitions & Chemical Command
Aberdeen Proving Ground, Maryland 21010-5423

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Although large extensional flow components occur in many technological processes of liquids, there is no currently suitable device to measure the elongational properties of polymer solutions. This report describes a possible method of inferring extensional fluid properties by determining the nonlinear, time-dependent mechanical properties of concentrated solutions of polymers from stress relaxation in torsion measurements. This method is based on the BKZ model of an isothermal elastic fluid with an elastic potential function of the Valanis Landel type.

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PREFACE

This work was performed under Contract DAAK-11-83-C-0040, Phase I, Rheology of Dissemination. The work was started in June 1983 and completed in June 1984.

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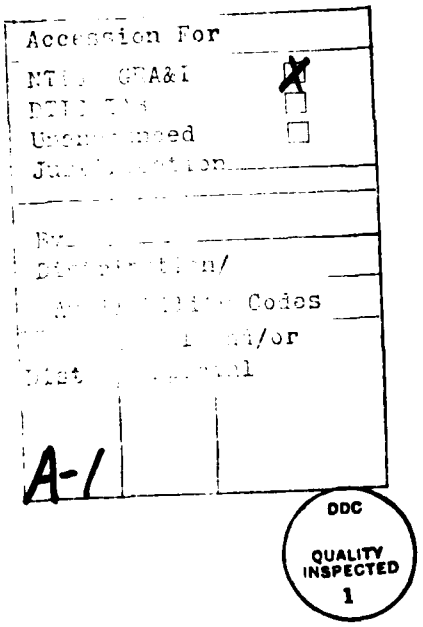

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RHEOLOGY OF DISSEMINATION

1. INTRODUCTION

The breakup of a mass of liquid injected into a high speed airstream is an extremely complex process. Even in the simplest cases, the disintegration of the fluid into a cloud of drops is not understood well enough to allow rational design and control of the process. For instance, methods of control of drop size and drop size distribution are yet to be developed. Although the mechanisms of breakup of the fluid are presently uncertain, nevertheless, it has been demonstrated that the addition by solution of small quantities of certain high polymeric materials can significantly affect the process of breakup of the mass of liquid. Consequently, investigation of the effects of polymeric additives is considered to be the most promising approach for developing a method of controlling the distribution of the resulting drop sizes.[1] Relatively little is known about the quantitative effects of polymer additives on drop size or even which polymers are most effective in controlling the breakup mechanism.

High speed photographs of the disintegration of a mass of liquid in a high speed airstream suggest that in the case of these polymer solutions, at least, the drop formation is caused by the extension of filaments of fluid or the inflation of sheets of fluid to a point where a mechanical instability causes breakup. Indeed, even qualitatively, the way in which breakup into droplets occurs seems to differ for pure solvents (with simple Newtonian properties) and polymer solutions (with time dependent, elastic, rheological properties). It seems clear that dissolving small quantities of high molecular weight polymers into a liquid can effectively control its breakup into drops in a high speed air stream and that this effect arises from the strong modification of the mechanical properties of the liquid induced by the polymer solute, particularly of the properties in extension. At this time, however, it is not clear what features of the extensional properties play the dominant role or how to measure them.

The project Rheology of Dissemination, contract DAAK 11-83-C-0040, is developing the rheology of polymer solutions necessary for understanding this process of the breakup of fluids in airstreams. In the year from July 1983 through June 1984 the activities of this project have centered on devising and demonstrating a method of evaluating the mechanical properties in extension of model polymer solutions using a commercially available rheometer. The objectives of Phase I of this contract, to develop the rheology necessary to describe the extensional flow behavior of high molecular weight solutions, is completed with this report.

2. THEORETICAL BASIS

The rheology of a material, that is, the mechanical behavior in flow, is most conveniently expressed in the form of a constitutive equation. The rheology of polymer solutions can be well modeled by using the so-called BKZ model which has been widely applied in the last decade to a variety of polymer solutions, polymer melts and rubbers.[2] This model expresses the stress at a point in the material in terms of a time integral over the history of deformation of the material point. In the case of isothermal flows of homogeneous incompressible fluids, the model may be summarized in the following equation:

$$S_{ij} = -p\delta_{ij} + 2\int_{-\infty}^{t} [U_1(B(t,\tau),\ t-\tau)\ B_{ij} - U_2(B(t,\tau),\ t-\tau)\ B_{ij}^{-1}]\ d\tau \qquad (1)$$

$$I = trB,\ II = trB^{-1},\ detB = 1$$

where S is true stress, p is an arbitrary scalar pressure, I and II are respectively the first and second scalar invariants of B, τ is a variable of integration which has the significance of time in the past with respect to t the present time and B is the left relative Cauchy-Green tensor. In this equation U is a scalar function of time and of the scalar deformation invariants of B and the partial derivatives of U with respect to the invariants I and II are indicated by subscripts 1 and 2, respectively. Notice that B and thus I and II are calculated from the deformation which maps the configuration at time τ into the configuration at time t and thus they are implicit functions of these times. The function U is constitutive, that is, it carries a complete description of the characteristic mechanical behavior of the material undergoing deformation. U has the character of a time-dependent elastic strain energy function and, in general, it must be measured for each material.

In principle, U (more precisely, its derivatives) can be measured from stress relaxation experiments for various values of I, II and t. To characterize the material in extensional flows, measurements would be made at pairs of values of I and II characteristic of simple extension. Stress relaxation experiments play a very fundamental role for BKZ materials. The information carried by the constitutive function U may also be expressed in terms of stress relaxation functions. Let $S_{SR}(B,t)$ represent the stress relaxation function, that is, the residual stress in a specimen at a time t after being subjected to and held at a deformation (represented by tensor B) from a stress-free relaxed state. Then equation (1) may be rewritten in terms of this stress relaxation function as follows:

$$S(t) = -pI + \int_{-\infty}^{t} S_{SR}(B(t,\tau),\ t-\tau)\ d\tau \qquad (2)$$

This equation says that with any history of deformation the present stress in a material is a superposition of stress relaxation functions for deformations representing the change in configuration from times in the past to the present and for relaxation times of the corresponding time interval. In other words, one can completely specify the mechanical behavior of a BKZ material by measuring the stress relaxation function for all times and all deformations.

The stress relaxation function as a function of deformation for a fixed relaxation time is known as an isochrone. An isochrone of a BKZ material has the character of a strain energy function of finite elasticity theory. The mechanical properties of a BKZ material are determined by a time dependent strain energy function corresponding to a complete set of isochrones. Thus the ideas of finite elasticity theory can be applied.

In finite elasticity theory, the properties of a material are given through a strain energy function. In general, the behavior of the material in extension cannot be inferred from its behavior in shear. Valanis and Landel have proposed a special form of strain energy function which they showed to model accurately the behavior of natural rubber and other polymeric elastomers.[3] The Valanis-Landel form of elastic strain energy function carries the constitutive information of a material in the form of a single scalar function of one variable. This function can be evaluated either from shear measurements or from extensional measurements and thus, for a Valanis-Landel material the behavior in extension can be inferred from the behavior in shear.

The strain energy function of a Valanis-Landel elastic material, W, is given as follows:

$$W = w(\lambda) + w(\mu) + w(\nu)$$
$$\lambda\mu\nu = 1 \qquad (3)$$

where w(.) is the constitutive functional (we shall call the V-L function) and λ, μ, ν are stretches in the three principal directions. The second of equations (3) expresses the fact that the material is considered incompressible.

To produce simple torsion in a right circular cylinder of an incompressible elastic material, it has been shown that a moment Γ must be applied to the circular ends of the sample:

$$T = 4\pi\psi \int_0^R (W_1 + W_2)\, r^3\, dr \tag{4}$$

and in addition a normal force, N, must be applied to the ends and parallel to the axis of the cylinder.

$$N = -2\pi\psi^2 \int_0^R (W_1 + 2W_2)\, r^3\, dr \tag{5}$$

Note that N is usually compressive and negative. Here, ψ is the angle of twist per unit axial length, R is the radius of the cylinder and the subscripts 1 and 2 indicate partial derivatives of the strain energy function W with respect to the invariants I and II, respectively. When these equations are put in terms of the V-L function, they become

$$T = 2\pi\psi \int_0^R \frac{\lambda^2}{(\lambda^4-1)} [\lambda w'(\lambda) - 1/\lambda\, w'(1/\lambda)]\, r^3\, dr \tag{6}$$

$$N = -\pi\psi^2 \int_0^R \frac{\lambda^2}{(\lambda^2-1)(\lambda^4-1)} [(\lambda^2 - 2)\, \lambda w'(\lambda) - (2\lambda^2 - 1)\, 1/\lambda\, w'(1/\lambda)]\, r^3\, dr \tag{7}$$

where λ is a principal stretch given by

$$\lambda = \tfrac{1}{2}((\psi^2 R^2 + 4)^{\frac{1}{2}} + \psi R) \tag{8}$$

In order to use these equations to evaluate the V-L function it is necessary to find values of stress at a point from the torque and normal force acting on the ends of the cylinder. A procedure developed by Penn and Kearsley [4] will accomplish this. Using this procedure and using equations (6) and (7) one obtains

$$\lambda w'(\lambda) - 1/\lambda\, w'(1/\lambda) = \frac{1}{2\pi\psi R^4} \frac{\lambda^4 - 1}{\lambda^2} (3T + \psi T_\psi) \tag{9}$$

$$(\lambda^2 - 2)\,\lambda w'(\lambda) - (2\lambda^2 - 1)\,1/\lambda\, w'(1/\lambda) = -\frac{1}{\pi\psi^2 R^4}\frac{(\lambda^2-1)(\lambda^4-1)}{\lambda^2}(2N + \psi N_\psi) \qquad (10)$$

where T_ψ and N_ψ are the slopes of the isochrones of T and N plotted against twist. ψ From these equations it is easy to solve for the derivative of the V-L function to get

$$\lambda w'(\lambda) = \frac{\lambda^2-1}{2\pi\gamma^2 R^2 \lambda^2}[(2\lambda^2-1)M + 2(\lambda^2-1)P] \qquad (11)$$

$$\frac{1}{\lambda} w'(\frac{1}{\lambda}) = \frac{\lambda^2-1}{2\pi\gamma^2 R^2 \lambda^2}[(\lambda^2-2)M + 2(\lambda^2-1)P] \qquad (12)$$

where

$$M = (3 + \frac{\partial \log T}{\partial \log \gamma})\frac{\gamma T}{R} \qquad (13)$$

$$P = (2 + \frac{\partial \log N}{\partial \log \gamma})\, N \qquad (14)$$

which is valid for values of stretch, λ ,and shear, γ ,given by

$$\lambda = \frac{1}{2}((\gamma^2 + 4)^{\frac{1}{2}} + \gamma),\ \gamma = \psi R \qquad (15)$$

In modelling a polymer solution as a BKZ fluid with constitutive function U(I,II,t) of the Valanis-Landel type we take the isochrones of stress relaxation to correspond to an elastic strain energy. The V-L function then must be taken as a function of time as well as stretch. Then stress relaxation experiments of a right circular cylinder in torsion may be used as shown above to calculate the V-L function. Each set of isochrones of torque and normal force for a fixed relaxation time can be analysed as for an elastic material. By repeating this procedure for a range of relaxation times

it is possible to find a function of two variables, $\lambda W'(\lambda)$, which completely characterizes the non-linear, time-dependent, mechanical behavior of the solution.

When the V-L function is measured for all relevant values of stretch and time by this method (or any other method) the stress can be calculated for any deformation history. For instance, if the length L of a strand of fluid were to undergo a stretch given by L(t) the force F(t) required to produce this stretch can be calculated from

$$F(t) = A(t) \int_{-\infty}^{t} [\lambda W'(\lambda, t-\tau) - \lambda^{-\frac{1}{2}} W'(\lambda^{-\frac{1}{2}}, t-\tau)] \, d\tau \qquad (16)$$

$$\lambda = L(t)/L(\tau)$$

where F(t) is the force extending the strand at time t, L(t) is the length of the strand and A(t) is the cross-sectional area. To use this equation, the history of the length of the strand is observed from an equilibrium rest position up to time t.

The integral in this equation may be looked upon as a superposition of stress relaxation functions for the fluid in extension. These stress relaxation curves are calculated with the following equation:

$$S_{SR}(t) = \lambda W'(\lambda, t) - \lambda^{-\frac{1}{2}} W'(\lambda^{-\frac{1}{2}}, t) \qquad (17)$$

where $S_{SR}(t)$ is the stress remaining after time t in a strand of fluid stretched and held at a stretch of λ . Thus if we construct a complete set of stress relaxation curves for a range of extensions and times, we will be able to calculate the stress resulting from any history of strain within the same range of variables. We will in fact construct such a set of stress relaxation curves from the V-L functions calculated from data of torsion.

3. EXPERIMENTAL DETAILS

3.1 Equipment

The principal data used were measurements of stress relaxation in torsion using a Rheometrics Mechanical Spectometer RMS-7200. Details of the calibrations and measurement procedures have been reported previously.[5] Most of the stress relaxation data was taken with a parallel plate geometry between circular plates of diameter 7.22cm. A relief well and outer retaining wall for catching extruded excess fluid on the lower plate had been suspected of introducing some error in data of the previous report and was eliminated for all the measurements reported here. Some stress relaxation data and some steady state shear data were taken with a cone and plate geometry. The cone used in these measurements had an angle of .04 radians.

3.2 Solutions

Data was run on solutions of K-125, a copolymer of 20% ethyl butyl acrylate and 80% poly methyl methacrylate, in di ethyl malonate (DEM). The concentrations used were dictated by the practical limitations of the Rheometrics device. If the solutions were too concentrated, it became impossible to load the test sample into the small cylindrical volume needed without introducing large air bubbles. On the other hand, solutions which were too dilute did not generate sufficient forces and torques during deformation to allow accurate measurements. For the machine used in this report the convenient concentrations of K-125 ranged roughly between 10 to 15 grams of polymer per deciliter of solvent. Difficulties in dissolving these high concentrations and in obtaining a homogeneous material and the resolution of these problems are discussed in a previous report.[5]

Solutions were kept in tightly sealed jars to avoid loss of solvent. Data were taken within eight hours of loading the rheometer since the sample lost solvent with time, particularly at the outer edge where exposure to the atmosphere occured. Measurements repeated within this time period gave results within the reproducibility of successive measurements.

Table 1 lists the solutions for which measurements were attempted. Only for the four highest concentrations was it possible to obtain data sufficient to calculate the V-L function.

Table 1. Composition of solutions

Designation	K-125 lot #	grams/dl.
K-5	6-4077	5.11
K-8	6-4077	7.66
K-10	6-4077	10.07
K-12	3-6326	11.72
K-13	6-4077	12.89
K-14	3-6326	14.36
K-15	3-6326	15.01

The results of gel permeation chromatography indicate that there was a probably some difference in molecular weight distribution between the two lots of K-125. The copolymer K-125 of lot #6-4077 had a weight-average molecular weight (in millions) of 1.45 and a number-average molecular weight of 0.528 while that of lot #3-6326 had corresponding molecular weights of 1.35 and 0.590 respectively. With only one exception data used for the examination of concentration dependence of stress relaxation was taken on solutions of copolymer from lot #3-6326. Molecular weight differences were not considered in the analysis.

3.3 Procedure

Loading the test sample into the Rheometrics required certain precautions in order to avoid air bubbles or irregular edge conditions. Details of these are described in a previous report as are the other details of the experimental procedures. For each solution it was necessary to do about six relaxations at each value of shear to map out a complete relaxation curve. Considerable patience was required.

Table 2 lists for each solution the values of maximum shear for which relaxation curves were measured.

Table 2. Values of maximum shear

Solution	Maximum Shears.....
K-10	7.64, 9.90
K-13	0.85, 1.21, 1.56, 1.81, 2.41, 2.66, 3.80, 6.03, 6.75, 6.91, 8.94, 9.10
K-15	0.66, 0.70, 2.60, 3.98, 5.19, 7.83, 9.04
K-12	5.72, 7.55, 9.95, 12.74, 14.91
K-14	1.68, 2.40, 3.60, 4.79, 5.98, 7.16, 8.52, 10.79

4. CALCULATIONS

4.1 The V-L Function

From the data on torsion for each solution the V-L function is constructed in the following way:

a. Plots are made on log-log paper of the measured values of torque, T, and normal force, N, versus the shear, for each relaxation time recorded. These plots are used to construct smooth isochrones.

b. The slopes of these isochrones are measured at points distributed along the plots, that is, for a set of values of shear.

c. From the values and slopes of these isochrones the function $\lambda w'(\lambda)$, where $w(.)$ is the V-L function, is calculated for a set of values of stretch using equations **(11) to (15).**

4.2 Stress Relaxation in Extension

Since by definition $\lambda\, w'(\lambda)$ is zero at a stretch of one it is not convenient to plot the logarithm of $\lambda w'(\lambda)$. The results above are therefore most conveniently plotted on semi-log paper versus the logarithm of stretch. Stress relaxation in extension can be calculated through equation (2.17) with data taken from smoothed curves based on such plots. The calculation of $\lambda w'(\lambda)$ for values of λ less than one usually involves small differences of measured quantities and is only roughly determined. However, these values contribute only a small term to the calculated stress relaxation and thus pose no problem.

It is actually more convenient to display the stress relaxation data in the form of a reduced stress which does not go to zero as the stretch goes to one. The reduced stress for extension is defined as follows:

$$S_{RED} = \frac{\lambda}{\lambda^3 - 1} S_{SR} \qquad (18)$$

Figure 1 shows the calculated reduced extensional stress-relaxation curve for solution K-14.

4.3 Concentration Superposition

Zapas and Phillips[6] have shown that for concentrated solutions of polymers exhibiting strongly non-linear behavior it is possible to account for concentration effects by superposing relaxation curves for a given deformation of solutions of different concentrations. Following their procedures the extensional stress

relaxation curves for the four solutions with concentrations ranging between about 8.7 and 15 grams of K-125 per deciliter of DEM were reduced and combined to form a master curve. Figure 1 is that mastercurve in which all the data have been superposed on the reduced stress relaxation curves in extension of the solution K-14, that is, they have been reduced to a concentration of 14.36 grams/dl.

This reduction was accomplished in the following way. The calculated extensional reduced (equation (17)) stress relaxation curve of each solution is shifted vertically on a log-log plot versus relaxation time by an amount corresponding to the square of the ratio of 14.36 (the standard concentration, in this case) to the concentration of the solution. The relaxation curve is then shifted horizontally to superpose with the data for solution K-14, the solution of standard concentration. The amount of horizontal shift (time-concentration shift) necessary for superposition is recorded.

When the data is available, a rough check on the time-concentration shift can be made with zero shear viscosity data of solutions of different concentrations. In Figure 2 we have plotted zero shear viscosity estimated from steady shear data on the various concentrations using a cone and plate geometry. Also included in this plot are some data for solutions too dilute to obtain stress relaxation data. The time-concentration shift for a solution of any concentration within this range can be found with reasonable accuracy by dividing the viscosity read off Figure 2 by the viscosity at the standard concentration and then dividing this result by the square of the concentrations. An example of a reduction done in this way can be read off Figure 1 for a solution of concentration 4 grams/dl. by referring to the stress scale on the right and the time scale on the top. The extremely low values of reduced force associated with this reduced relaxation curve indicate the difficulty of measuring these quantities directly.

4.4 Consistency Checks

We have indicated above how the viscosity data can be used to check the reasonableness of the concentration-time shift. In addition, the stress relaxation data taken with cone and plate geometry can be used to check the consistancy of the Rheometrics measurements of torque and normal force. In the first place, the normal force and torque for stress relaxation in torsion in the cone and plate geometry are related. The relation between them, which was used to check for errors in the apparatus, is the following:

$$T/N = 4R/3\gamma \qquad (19)$$

Another check is possible by comparing torque relaxation data between cone and plate measurements and parallel plate measurements.

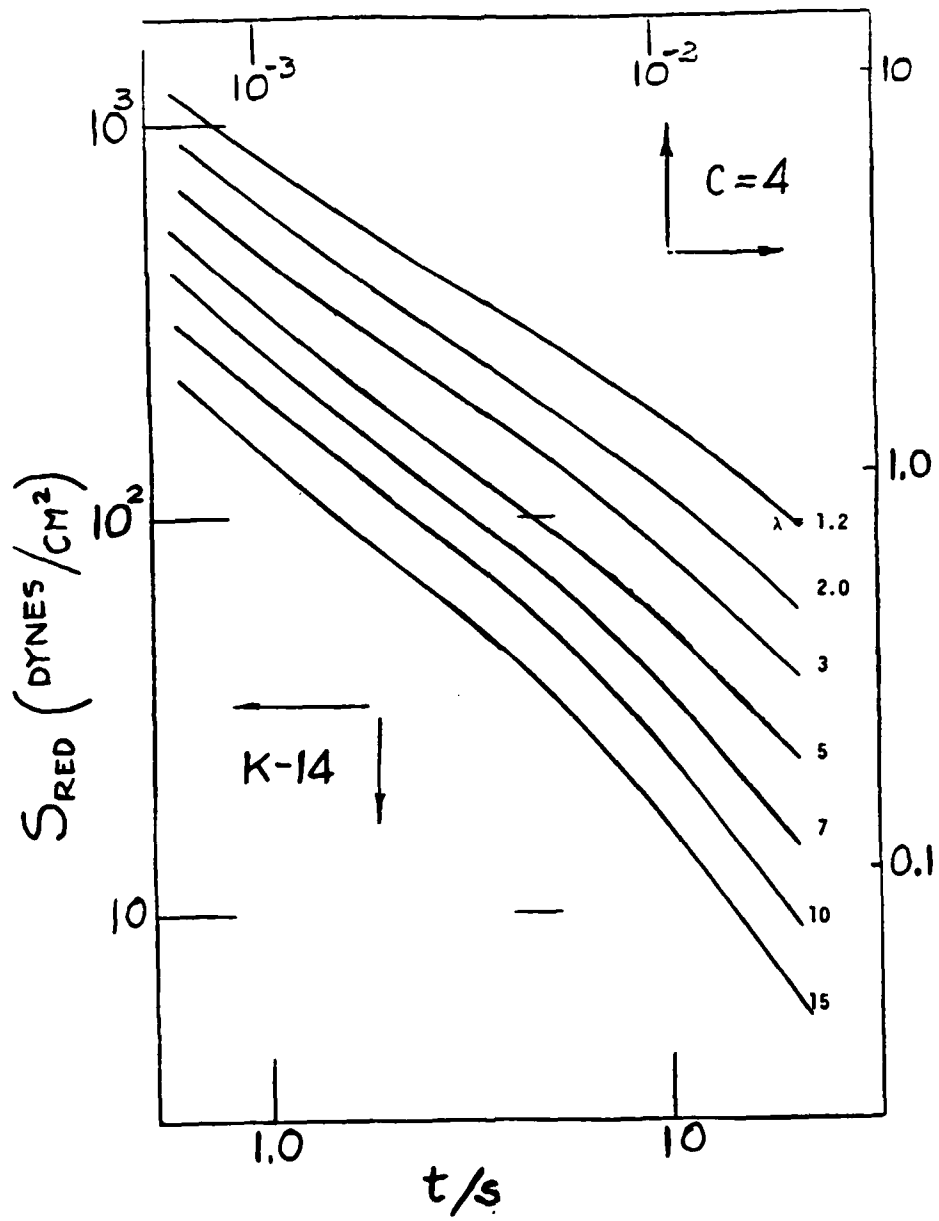

Figure 1. Reduced stress in extension versus time - logarithmic plot. Standard solution K-14 has a concentration of 14.36 g/dl. Scales to top and right are for concentration of 4 g/dl.

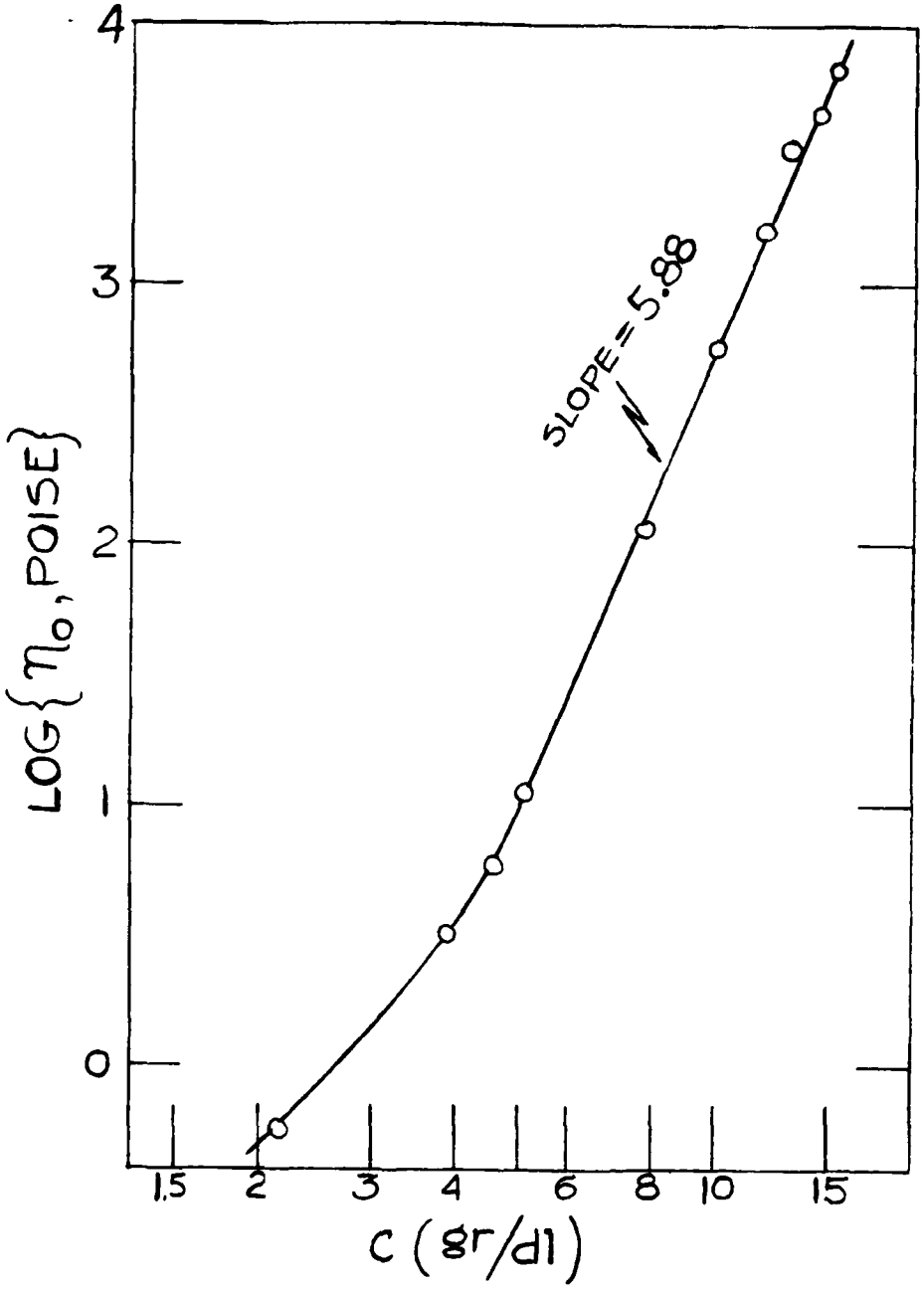

Figure 2. Zero shear viscosity versus concentration - logarithmic plot.

The cone and plate isochrones of torque can be related to the parallel plate isochrones of torque by the equation

$$3T^{CP}(\gamma, t) = 3T^{PP}(\gamma, t) + \gamma T^{PP}(\gamma, t) \qquad (20)$$

where the superscripts CP and PP refer to data for cone and plate and parallel plate geometries, respectively. The subscript indicates differentiation and therefore the slope of the isochrone. This relation is a rather sensitive check on the relative accuracy of the measurements. It can be derived for any constitutive equation of the BKZ type.

The equation above can easily be inverted to give the equation

$$T^{PP}(\gamma, t) = \frac{3}{\gamma^3} \int_0^{\gamma} x^2 T^{CP}(x, t)\, dx \qquad (21)$$

which can be used to calculate the parallel plate isochrones from a weighted integral of the cone and plate isochrones. There is often an advantage to integrating experimental data rather than differentiating it.

5. CONCLUSIONS AND PLANS

A method of determining the nonlinear, time dependent mechanical properties of concentrated solutions of polymers from stress relaxation in torsion has been demonstrated. This method is based on a BKZ model of an isothermal elastic fluid with an elastic potential function of the Valanis Landel type.

Families of stress relaxation functions in extension have been calculated with the method for four solutions of copolymer K-125 in di ethyl malonate. The constraints and limitations of the Rheometrics apparatus for this purpose have been explored. Concentrations of these solutions for which it is possible to make measurements adequate for this purpose ranged between 10 and 15 grams of solute per deciliter of solvent.

Several checks have been made on the consistency of these stress relaxation measurements. Data have been taken on stress relaxation with cone and plate geometry and the normal stress has been shown to be consistent with the torque. The torque of parallel plate measurements has been shown to be consistent with the torque of cone and plate measurements.

A method of superposing relaxation functions of solutions of differing concentrations has been demonstrated. From the master curve found through this superposition it is possible to interpolate or extrapolate to produce a relaxation curve for a solution of K-125 of any concentration arbitrary within a wide range.

The time-concentration shift determined in forming the master curve was found to be consistent with estimates of zero shear viscosity as a function of concentration based on measurements of viscosity as a function of rate of shear.

Experimental and theoretical studies of some convenient extensional flow will now be pursued in order to verify the applicability of these methods and to gain insight.

The formulation of some convenient model of the rapid extension of a filament of elastic fluid leading to breakup into drops will be attempted in light of the present understanding of the mechanical properties of these solutions with the idea of pinpointing the features of the extensional relaxation curve which will most strongly influence the drop forming processes.

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